Lifetime of a K-shell vacancy in Carbon by $1s \rightarrow 2p$ photo-excitation of C^+

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Femtosecond lifetimes for K-shell vacancy states in atomic carbon have been determined by measurement of the natural width of the $1s \rightarrow 2p$ photo-excited states of C^+ ions. The states produced by photoionization of atomic carbon are identical to those of a carbon ion (C^+) K-shell excited by a photon: $1s2s^22p^2\ ^2D, ^{2,4}P, ^2S$ autoionizing states occur in both cases. These hole-states may stabilize by emission of one or more electrons to produce multiply charged carbon ions. We report here the first measurements of the lifetime for the $1s2s^22p^2\ ^2P$ and $1s2s^22p^2\ ^2D$ autoionizing states of C^+, which are found to be 12.2 ± 0.9 fs and 6.5 ± 0.9 fs respectively. Knowledge of such lifetimes is important for comparative studies of the widths of K-shell vacancies in hydrocarbon molecules, for benchmarking theory, and for interpreting satellite x-ray spectra from astrophysical sources such as x-ray binaries. A combined theoretical investigation (using state-of-the-art techniques) and experimental measurements (performed at the Advanced Light Source in Berkeley) illustrate suitable agreement.

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Carbon is ubiquitous in nature and is the building block of life. This atom in its various stages of ionization has relatively few electrons, and is thus amenable to theoretical study. Despite the importance of the neutral carbon atom, it is surprising that there are no detailed measurements of inner-shell photoionization or photoexcitation processes, and that the lifetime of a K-shell vacancy has not been experimentally determined. The major difficulty is that free carbon atoms cannot readily be made, and various attempts to produce them generally result in neutral dimers and clusters. In the present investigation a different experimental approach has been followed using a photon-ion merged-beams apparatus at the Advanced Light Source to study inner-shell photoexcitation and photoionization of the carbon C^+ ion. In this Letter the first measurements of the lifetimes for the $1s2s^22p^2\ ^2P$ and $1s2s^22p^2\ ^2D$ autoionizing states of C^+ are reported.

Understanding the chemical abundances of the universe relies in large measure on spectroscopic observations of cosmic plasmas. Quantitative information about the cosmos is the result of observation from ground- and satellite-based observatories. In particular, the recently launched x-ray satellites *Chandra* and the *XMM-Newton* satellites are currently providing a wealth of x-ray spectra of astronomical objects. There is a serious lack of adequate atomic data needed for the interpretation of these spectra [1]. Spectroscopy in the soft x-ray region (5-45 Å) including K-shell transitions of C, N, O, Ne, S and Si, and the L-shell transitions of Fe and Ni, provides a valuable probe of the extreme environments in active galactic nuclei (AGN's), x-ray binary systems and cataclysmic variables. A limited body of high quality theoretical or experimental work exists for inner shell photoexcited neutral, singly, doubly or triply ionized species of relevance to astrophysical applications [2–6], but such data are insufficient to meet the needs of the astrophysics models which require many hundreds of cross sections for several different atomic species. Modellers therefore have to resort to using crude models with their inherent limi-

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tations [7].

The primary goal of the present research is to provide benchmark theoretical and experimental values for the energies and lifetimes of autoionizing states of the C^+ ion in the vicinity of the K-edge. In the C^+ ion complex, promotion of the inner-most K-shell (1s) electron to the L-shell (2p) by a photon produces autoionizing states via the processes

$$h\nu + C^+(1s^2 2s^2 2p\ ^2P^o) \longrightarrow C^+(1s2s^2 2p^2\ ^2P, ^2D, ^2S) \downarrow C^{2+}(1s^2 2s^2\ ^1S) + e^-. \quad (1)$$

These $C^+(1s2s^2 2p^2\ ^2P, ^2D, ^2S)$ states may also be created in neutral carbon via the processes

$$h\nu + C(1s^2 2s^2 2p^2\ ^3P) \rightarrow C(1s2s^2 2p^3\ ^3P^o, ^3D^o, ^3S^o) \searrow \downarrow C^+(1s2s^2 2p^2\ ^2L) + e^-, \quad (2)$$

where the same intermediate vacancy state is produced in both processes. Values of the total angular momentum L that are allowed in (2) correspond to the ^2S, ^2P and ^2D terms of the residual C^+ ion. Similarly for an initial $1s^2 2s2p^2(^3P)\ ^4P$ metastable state of the carbon ion, $C^+(1s2s2p^3\ ^4D^o, ^4P^o, ^4S^o)$ autoionization states can be formed in the photoionization process. Metastable states of the C^+ ion that may contaminate the beam can then be detected if such autoionizing states are present in the final results.

Photoionization calculations in LS–coupling were performed on C^+ using the R-matrix method [8]. An appropriate number of C^{2+} target states (135 levels) were included in the R-matrix plus pseudo-state close-coupling calculations. A suitably chosen n=4 basis set of C^{2+} orbitals was used to represent the target wavefunctions [9, 10]. Double-electron promotions from specific base configuration sets were used to describe the appropriate scattering wavefunction in the R-matrix calculations. The results for properties of the $C^+(1s2s^2 2p^2\ ^2D, ^2P, ^2S)$ autoionization states (1) are presented in Table I.

Experiments were performed on beam line 10.0.1.2 at the Advanced Light Source (ALS) in Berkeley, California. The ultra-high brightness of an undulator beam line was required to obtain sufficient photon intensity with high spectral resolution. A photon beam from the ALS was merged over a path length of approximately 100 cm with a well-collimated energy- and mass/charge-selected ion beam from a small accelerator. This merged-beam technique was first used by Lyon and co-workers [11], and has been applied more recently by several other groups [12–14]. It has proved successful in benchmarking theory in recent absolute high-resolution photoionization measurements on several other ionic species [15–17].

K-shell photo-absorption experiments have been carried out on various complexes using a laser-produced plasma which provides a continuum spectrum to backlight a second laser-produced plasma containing ions of the species of interest [18, 19]. This technique is useful for obtaining absorption spectra over a wide energy range but results are difficult to interpret due to ions being distributed over various charge states in the ground state and metastable states. The presence of a plasma can also affect energy levels. Absolute cross sections cannot be obtained and spectral resolution is limited. Results for $C^+(1s2s^2 2p^2\ ^2D, ^2P, ^2S)$ autoionizing states determined by this technique [20] are presented in Table I.

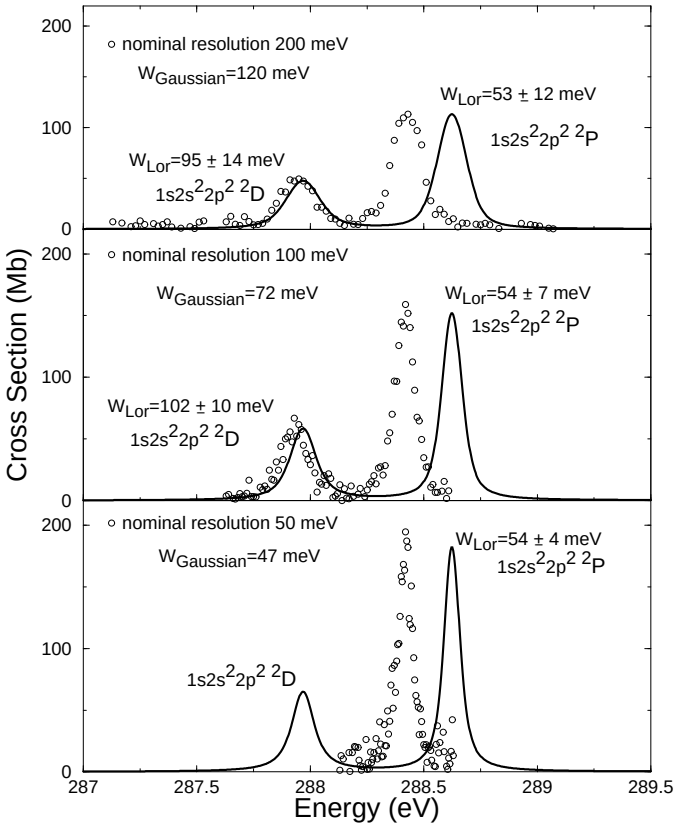

FIG. 1: Cross sections in megabarns (Mb) as a function of photon energy in eV for 1s → 2p photo-excitation of the C^+ ion are shown. Solid line: theoretical results, using basis B [10], convoluted with an appropriate instrumental resolution FWHM Gaussian of 120 meV, 72 meV and 47 meV. The widths W_{Lor} and $W_{Gaussian}$ for the 1s → 2p photo-excited C^+ states are extracted from the measurements by fitting Voigt profiles to the observed peaks. These fits provide an instrumental (Gaussian) and a (Lorentzian) linewidth for each peak. The photoion yield experimental results were normalized to the theoretical values.

The ALS merged beam set-up was used to study the 1s → 2p photoexcitation processes in the carbon ion for the energy region 287 eV – 291 eV, where autoionization states were expected to be located. The ion beam was charge-state analyzed after the interaction region: the primary C^+ ion beam was collected in a Faraday cup, while the product C^{2+} ions were counted by a calibrated

single-particle detector. The photon beam was time modulated to subtract background mainly resulting from ions which have changed their charge state in collisions with residual gas. Typical ion-beam currents were 30 to 40 nA in the primary ion current, the photon flux with a bandwidth $E/\Delta E = 1000$ was 7.5×10^{11} photons/s at 300 eV, and count rates were up to 60 Hz from the energy-labeled collision region of 29.4 cm length.

Experimental results are illustrated in Fig. 1, at three different spectral resolutions for two of the peaks found in the spectra for photons incident on C^+ ions in the energy range 287 eV - 289.5 eV. Only the larger of the two peaks could be measured in a reasonable time at the highest spectral resolution. These peaks were fitted with a Voigt profile, which is a convolution of a Gaussian and a Lorentzian profile. The Gaussian is assigned to the instrumental profile, and the Lorentzian to the natural width. Both peaks were constrained to have the same Gaussian width for a given nominal resolving power. Photon energies were calibrated relative to a photo-absorption measurement of the carbon $1s \rightarrow \pi^*$ resonance in CO, whose energy is known from electron-energy-loss spectroscopy to be 287.40 eV [21, 22]. The experimental energies were corrected for the Doppler-shift of the moving ions, and the energy scale was determined relative to photo-absorption in CO [21]. Allowance was made for possible non-linearities in the monochromator energy scale and for an uncertainty of 20 meV in the original measurement of the $1s \rightarrow \pi^*$ resonance in CO by Brion and co-workers [21]. This leads to an uncertainty of $\pm$ 200 meV in the present experimental energies. The shift from experiment in the theoretical energy peaks in Fig. 1, we attribute to the limitations of the basis set in representing electron correlation.

The same natural width was obtained for a given peak at the different resolutions, but with decreasing uncertainty as the spectral resolution improved, providing confidence in the results. The final measurement for the intrinsic linewidth Γ of the $1s2s^22p^2\ ^2P$ K-shell vacancy state in the C^+ ion, at 288.43 eV was 54 meV $\pm$ 4 meV. This value is in excellent agreement with the present theoretical values of 55 meV and 56 meV determined from the R-matrix method, and with other theoretical estimates; 52 meV [23, 24], 56 meV [25, 26] and 53 meV [27]. For the lower-energy peak, located at 287.94 eV and attributed to the $1s2s^22p^2\ ^2D$ K-shell vacancy, an experimental value of 102 $\pm$ 10 meV was determined for the linewidth, in harmony with the present theoretical estimates of 100 meV and 102 meV (Table I : R-matrix).

The lifetimes or the total widths for two of the C^+ autoionization states, $1s2s^22p^2\ ^2D, ^2P$, associated with the $1s \rightarrow 2p$ photo-excitation process were measured in the present work, providing a quantitative result for the lifetime of the vacancy produced by removing a K-shell electron from the neutral carbon atom. The intrinsic linewidth Γ is almost completely determined by autoionization. It was converted to a lifetime τ using the Heisenberg uncertainty principle: $\Gamma\tau = 658$ meV fs. The strongest peak in the spectra observed at 288.43 eV is due to the $C^+(1s2s^22p^2\ ^2P)$ K-shell vacancy state and determined experimentally to have a lifetime of 12.2 $\pm$ 0.9 fs. The lower-energy peak located at 287.94 eV, due to the $C^+(1s2s^22p^2\ ^2D)$ K-shell vacancy state was found experimentally to have a lifetime of 6.5 $\pm$ 0.9 fs. For these same states, it is seen that there is harmony between the experimental lifetimes of 12.2 $\pm$ 0.9 fs and 6.5 $\pm$ 0.9 fs and the R-matrix theoretical values of 12 fs and 6.6 fs, using basis A [9], and 11.8 fs and 6.5 fs using basis B [10]. For the energies of these two C^+ K-shell vacancy states (as illustrated from the results presented in Table I), basis B provides more accurate values. Table I includes experimental and theoretical results for the $C^+(1s2s^22p^2\ ^2S)$ K-shell vacancy state. From our investigations the C^+ K-shell vacancy state was observed experimentally at an energy of 289.90 eV $\pm$ 0.2 eV in accord with theoretical predictions of 289.99 eV (basis A) and 289.96 eV (basis B). This will be discussed in a future more-detailed paper on photoexcitation of carbon ions.

Theoretical Auger widths and fluorescence yields for a K-shell vacancy produced in a free carbon atom may readily be determined [1, 7, 23, 28]; however, until now there have been no measurements. Photoionization of a molecular species is often compromised by several factors, including post-collision interactions. The experimental method reported here does not suffer from post-collision-interaction (PCI) effects, as there are no slow electrons to influence the line shape.

Coville and Thomas [25] in their early work list both theoretical and experimental results for a wide variety of carbon-containing molecules. A notable absence is that of an experimental value for the free carbon atom. Two features are apparent from their work, first there is significant disagreement between experiment and theory, and secondly the linewidth for a carbon K vacancy in the molecular species studied are significantly larger (a factor of two) than that of the $1s2s^22p^2\ ^2P$ K-shell vacancy state in C^+. The present work and that of recent measurements on the photo-electron spectrum in CH_4 [29] and CO_2 [30] confirm this. Measurements of the intrinsic linewidths Γ depend on the photon energy. This is attributed to post-collision interaction effects, yielding values ranging from 93-95 meV in CH_4 to 99 meV in CO_2 at a photon energy of 330 eV.

In summary, lifetimes of C^+ K-shell vacancy states $1s2s^22p^2\ ^2P$ and $1s2s^22p^2\ ^2D$ have been measured by $1s \rightarrow 2p$ photo-excitation of C^+ ions to be 12.2 fs and 6.5 fs respectively. Photoion spectroscopy was used. This is the first time that lifetimes of an inner-shell vacancy in photo-excited C^+ ions have been measured. Theory and experiment have been combined to determine lifetimes, linewidths and energies of these states. Suitable accord is found between theoretical estimates determined using the R-matrix method and the ALS experimental work. These results are important for interpretation of x-ray satellite data, and for interpretation of molecular effects in K-shell vacancies produced in molecules con-

TABLE I: Autoionizing C^+ inner-shell excited states observed in the present experimental and theoretical work. The energies (eV) and autoionization linewidths Γ (meV) for each of the states found in the 1s → 2p inner-shell photo-excitation processes in C^+ are presented with earlier work.

State	E (eV)[a] (expt)	E (eV)[b] (expt)	E (eV)[c] (expt)	E (eV)[d] (MCDF)	E (eV)[e] (R-matrix)	E (eV)[f] (R-matrix)	Γ (meV)[g] (expt)	Γ (meV)[e] (R-matrix)	Γ (meV)[f] (R-matrix)	Γ (meV)[h] (theory)
$1s2s^22p^2\ ^2D$	287.94 ± 0.2	288.68 ± 0.7	287.90	288.26	287.99	287.96	102 ±10	100	102	85
$1s2s^22p^2\ ^2P$	288.43 ± 0.2	288.73 ± 0.7	288.53	288.28	288.65	288.62	54 ± 4	55	56	52
$1s2s^22p^2\ ^2S$	289.90 ± 0.2	290.98 ± 0.7	290.53	289.67	289.99	289.96	–	86	93	66

[a] Advanced Light Source, present work.
[b] Rødbro and co-workers[31].
[c] Jannitti and co-workers, expt, HF + relativistic corrections [20].
[d] Chen and Crasemann [28].
[e] R-matrix, n=4 basis A [9], present work.
[f] R-matrix, n=4 basis B [10], Table 4, present work.
[g] Advanced Light Source, present work.
[h] Estimated using the expressions from McGuire [23, 24].

taining carbon atoms.

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